California Environmental Protection Agency

Air Resources Board

Protocol for the Application and Ambient Air Monitoring of Benomyl In Merced/Madera/Fresno Counties During Winter, 2000

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Project No.
C99-108 Ambient/Application

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Protocol for the Application and Ambient
Air Monitoring of Benomyl
In Merced/Madera/Fresno Counties During Winter, 2000

I. Introduction

At the request (November 1, 1999 Memorandum, Helliker to Lloyd and November 23, 1999 Memorandum, Segawa to Castronovo) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of benomyl and it's breakdown products carbendazim and n-butyl isocyanate in Merced/Madera/Fresno Counties over a six week ambient monitoring program and over a three day application monitoring program. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions.... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of benomyl as a selective fungicide on almonds, grapes and stonefruits.

The sampling and analysis for benomyl will follow the procedures and quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version) which is included as Appendix A.

The draft method development results and "Standard Operating Procedures for the Analysis of Benomyl in Ambient Air" and the "Standard Operating Procedures for the Analysis of n-butyl isocyanate in Ambient Air" are included as Appendix B.

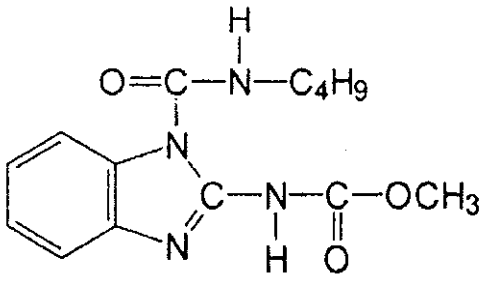
II. Chemical Properties of Benomyl

The following information on the physical/chemical properties of benomyl (Methyl 1-butylcarbamoyl-2-benzimidazolecarbamate) was obtained from the November 23, 1999 memorandum "Recommendation for Benomyl Monitoring for the Toxic Air Contaminant Program."

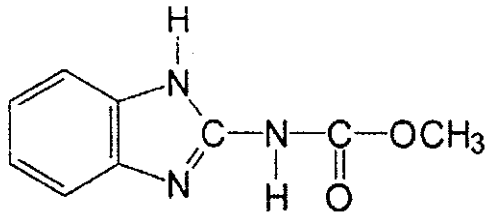
Pure benomyl (CAS: 17804-35-2) exists as colorless or white crystals with faint acrid odor. Benomyl has a molecular formula of $C_{14}H_{18}N_4O_3$ and a molecular weight of 290.3 g/mole. It has a water solubility of 2.8 mg/L at 25 °C (stable only at pH7), a Henry's Constant of 5.1×10^{-9} atm·m^3/mol at 25 °C, and a vapor pressure of approximately 3.73×10^{-8} mmHg at 25 °C.

In the environment, benomyl (figure 1a) decomposes by loss of the butylcarbamoyl group to form the relatively stable, strongly fungicidal methyl 2-benzimidazolecarbamate, also known as carbendazim (figure 1b) (Tomlin, 1994). In soil and water, benomyl rapidly converts to carbendazim and 2-aminobenzimidazole

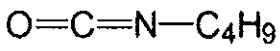
(Montgomery, 1997). Benomyl residues are relatively immobile in organic soils, and were detected only in the top four inches. At least two strains of fungi and four strains of bacteria demonstrated the ability to degrade benomyl to nonfungicidal compounds in loamy soils (Helweg, 1972).



(a) Benomyl



(b) Carbendazim



(c) Butyl isocyanate

Figure 1: The Chemical Structures of Benomyl, Carbendazim and n-Butyl Isocyanate

In laboratory studies under greenhouse conditions with temperatures ranging from 25°C to 40°C, benomyl decomposed to equimolar amounts of carbendazim and butyl isocyanate (BIC) (figure 1c) when mixed with water and introduced over a layer of basaltic gravel growing medium (Tang et al., 1993; Tang et al., 1992). BIC readily volatilized and was detected in the vapor phase, regardless of formulation. As temperature increased, the rate of BIC formation was enhanced in the early hours following application, especially when the dry flowable formulation was used (Tang, 1993). In a greenhouse study, BIC was detected in air samples collected from sealed glass dishes containing aqueous benomyl suspensions (Aragaki et al., 1994). Airborne concentrations of BIC would likely be lower under field conditions because of the dilution of open air (Tang, 1993).

Benomyl has an LC_{50} (96 hour) of 0.17 mg/L for rainbow trout, and 4.2 mg/L for goldfish. It is nontoxic to bees, with an oral and contact $LD_{50} > 10$ µg/bee (Tomlin, 1994).

III. Sampling

Samples will be collected by passing a measured volume of ambient air through two XAD-2 resin tubes that are mounted on a sampling tree as shown in Figure 2. One tube is used to collect benomyl and carbendazim and the other to collect n-butyl isocyanate. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until desorbed with organic solvent. The sampling flow rates of 2.5 liters per minute (Lpm) for benomyl/carbendazim and 30 cubic centimeters per minute (cc/min)[1] for BIC will be accurately measured and the sampling system operated continuously for 24 hours with the exact operating interval recorded in the logbook. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above rooftops for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Sacramento Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

A rotameter is used to control sample flow rates and two will be used per sampling tree. One rotameter will have a scale from 0-5 Lpm for benomyl/carbendazim and the other from 0-240 cc/min for BIC. The flow rates are set to 2.5 Lpm and 30 cc/min for benomyl/carbendazim and BIC, respectively, as measured using a digital mass flow meter (MFM) before the start of each sampling period. A MFM scaled from 0-5 Lpm is used for benomyl/carbendazim and a 0-100 cc/min MFM is used for BIC. The flow rate is checked, using the MFM, at the end of each period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. Any change in the flow rates will be recorded in the field logbook. The field logbook will also be used to record start and stop times, start and stop flow rates, start and stop counter readings, sample identifications and any other significant data.

Ambient Monitoring

The use maps for benomyl suggest that ambient monitoring should occur in Merced, Madera and Fresno Counties during the months of February through mid March. Four sampling sites will be selected in relatively high-population areas or in areas frequented by people. At each site, 24 discrete 24-hour samples will be taken during the sampling period. Background samples will be collected in an urban area distant to benomyl applications. Replicate (collocated) samples will be collected for six dates (each Wednesday) at each sampling location.

The sites selected by ARB personnel would be areas of Merced, Madera and Fresno Counties where farming of almonds and stonefruit is predominant. Sites are selected for their proximity to the fields with considerations for both accessibility and security of

1 Flow rate units of cc/min are equivalent to mLpm (milliliters per minute).

the sampling equipment. The towns chosen for sampling are Livingston, Merced, Madera, Fresno and Reedley. The sites are near areas of historical use of benomyl. ARB understands that DPR staff will verify and quantify the actual use of benomyl that takes place during the study when the information becomes available. DPR recommends a target 24-hour detection limit of 0.05 $\mu g/m^3$ for benomyl (sum of benomyl and carbendazim) and 8.1 $\mu g/m^3$ for n-butyl isocyanate.

ARB personnel will collect the samples over a six-week period from January 31 through March 10, 2000. 24-hour samples will be taken Monday through Friday (4 samples/week) at the flow rates of 2.5 Lpm and 30 cc/min for benomyl/carbendazim and BIC, respectively.

Application Monitoring

The use pattern for benomyl suggests that application-site monitoring should be conducted during the months of February or March in Merced, Madera, Fresno or Kern Counties, and that the monitoring be associated with applications of benomyl to almonds or grapes. Ideally, monitoring should occur at a site using the highest allowed rates of use (i.e., about 6.0 pounds per acre), however, growers typically apply 1 pound per acre for almonds, and 1-2 pounds per acre for grapes. Rarely do applications exceed 3 pounds per acre. Individual application monitoring schedules will vary based on the type and length of application but will follow the schedule guidelines outlined below in Table 1. Ideally, the monitoring study will include samples taken before, during and for approximately 72 hours following application.

TABLE 1. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	**Sample duration time**
Background (pre-application)	Minimum of 12 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) [1]
1 hour post-application	2 hours (or up to 1 hour before sunset) [1]
3 hour post-application	3 hours (or up to 1 hour before sunset) [1]
6 hour post-application	6 hours (or up to 1 hour before sunset) [1]
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

1 These sample duration times will be adjusted depending on length of application and time of sunset.

2 All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the

overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur all day long and over the course of two or more days. In these instances samples are collected during the first daily application, followed by a sample from end of application to 1 hour before sunset, followed by an overnight sample ending at either the start of application or 1 hour after sunrise the next morning (same for second or more application days). Following the end of the application, samples are collected according to the above schedule, starting with the 1-hour sample.

A minimum of eight samplers will be positioned, one at approximately the midpoint of each side of the field and one at each corner, if the field is roughly square. If the field shape is rectangular (e.g. long and narrow) then the 8 samplers will be located at regular intervals along the 2 long sides. A ninth sampler will be collocated at one position (downwind). Ideally, samplers should be placed at a minimum of 20 meters from the field. If possible the samplers will be spaced equidistant from the edges of the field. Since benomyl is extensively used in the area, background (before application) samples should collect enough volume to achieve the recommended target 24-hour quantitation limit of 0.05 $\mu g/m^3$ for benomyl, and 8.1 $\mu g/m^3$ for BIC. In all cases though, the minimum background sampling time should be 12 hours.

We will also provide in the monitoring report: 1) An accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, etc.; 3) meteorological data collected at a minimum of 15 minute intervals (averages) including wind speed, wind direction, humidity, air temperature, and comments regarding degree of cloud cover; 4) the elevation of each sampling station with respect to the field; and 5) the orientation of the field with respect to North (identified as either true or magnetic north). Samples collected during fog episodes will be designated as such.

IV. Analysis

The method development results and "Standard Operating Procedures for the Sampling and Analysis of Benomyl in Ambient Air" (SOP) are included as Appendix B. The procedures consist of ambient and application samples collected on XAD-2 resin cartridges with a flow rate of 2.5 Lpm. The exposed XAD-2 sorbent tubes are frozen until desorbed with 4 ml of acetonitrile. The injection volume is 100 µL. The reverse phase chromatographic method employs an isocratic mobile phase and a silica/C bonded stationary phase with ultraviolet spectrometric detection at 280 nm. The method detection limit (MDL) and estimated quantitation limit (EQL) for seven replicate spike samples are approximately 7.4 ng/mL and 37 ng/mL respectively. The MDL calculation is: MDL= 3.14(2.35 ng/mL) for n= 7 replicate spikes, and the EQL is: EQL= 5xMDL. The above MDL and EQL are estimates based on results presented in the attached SOP.

The method development results and "Standard Operating Procedures for the Sampling and Analysis of n-butyl isocyanate in Ambient Air" are included as Appendix B. The procedures consist of ambient and application samples collected on XAD-2 resin cartridges with a flow rate of 30 cc/min. The XAD is extracted with dichloromethane (DCM) and placed in a sonicator. The extraction solvent is filtered and the aliquot placed in a vial for analysis. The split injection volume is 1 μL. A gas chromatograph with a capillary column (5% phenylmethylpolysiloxane phase) and a quadrapole mass spectrometer (MS) is used for analysis. The MS detector is operated in selective ion monitoring mode. The method detection limit (MDL) and estimated quantitation limit (EQL) are approximately 0.02 μg per sample and 0.10 μg per sample respectively. The MDL calculation is: MDL= 3.14(s) for n= 7 replicate spikes, and the EQL is: EQL= 5xMDL. The above MDL and EQL are estimates based on results presented in the attached SOP.

VI. Quality Assurance

Field Quality Control for the ambient monitoring will include:

1) Ten field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) at six each for benomyl and four for BIC. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 2.5 Lpm and 30 cc/min for benomyl/carbendazim and BIC, respectively (i.e., collocated with a background sample). Three sample cartridges will be spiked at 2xEQL and three at 10xEQL for benomyl/carbendazim. Four sample cartridges will be spiked at 2xEQL for BIC.

2) Ten trip spikes prepared at the same level as the field spikes. Six trip spikes for benomyl and four for BIC.

3) Ten lab spikes prepared at the same level as the field and trip spikes. Six lab spikes for benomyl and four for BIC.

4) Replicate samples will be taken for six dates at each sampling location.

5) A Trip blank will be obtained each week of sampling.

Field Quality Control for the application monitoring will include:

1) Ten field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) at six each for benomyl and four for BIC. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 2.5 Lpm and 30 cc/min for benomyl/carbendazim and BIC, respectively (i.e., collocated

with a background sample). Three sample cartridges will be spiked at 2xEQL and three at 10xEQL for benomyl/carbendazim. Four sample cartridges will be spiked at 2xEQL for BIC.

2) Ten trip spikes prepared at the same level as the field spikes. Six trip spikes for benomyl and four for BIC.

3) Ten lab spikes prepared at the same level as the field and trip spikes. Six lab spikes for benomyl and four for BIC.

5) A Trip blank will be obtained.

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Flow controllers will be calibrated prior to and after sampling in the field.

VII. Personnel

ARB personnel will consist of Kevin Mongar and Oscar Lopez (Project Engineers) and Instrument Technicians from the Testing and Air Monitoring Central Sections of ARB.

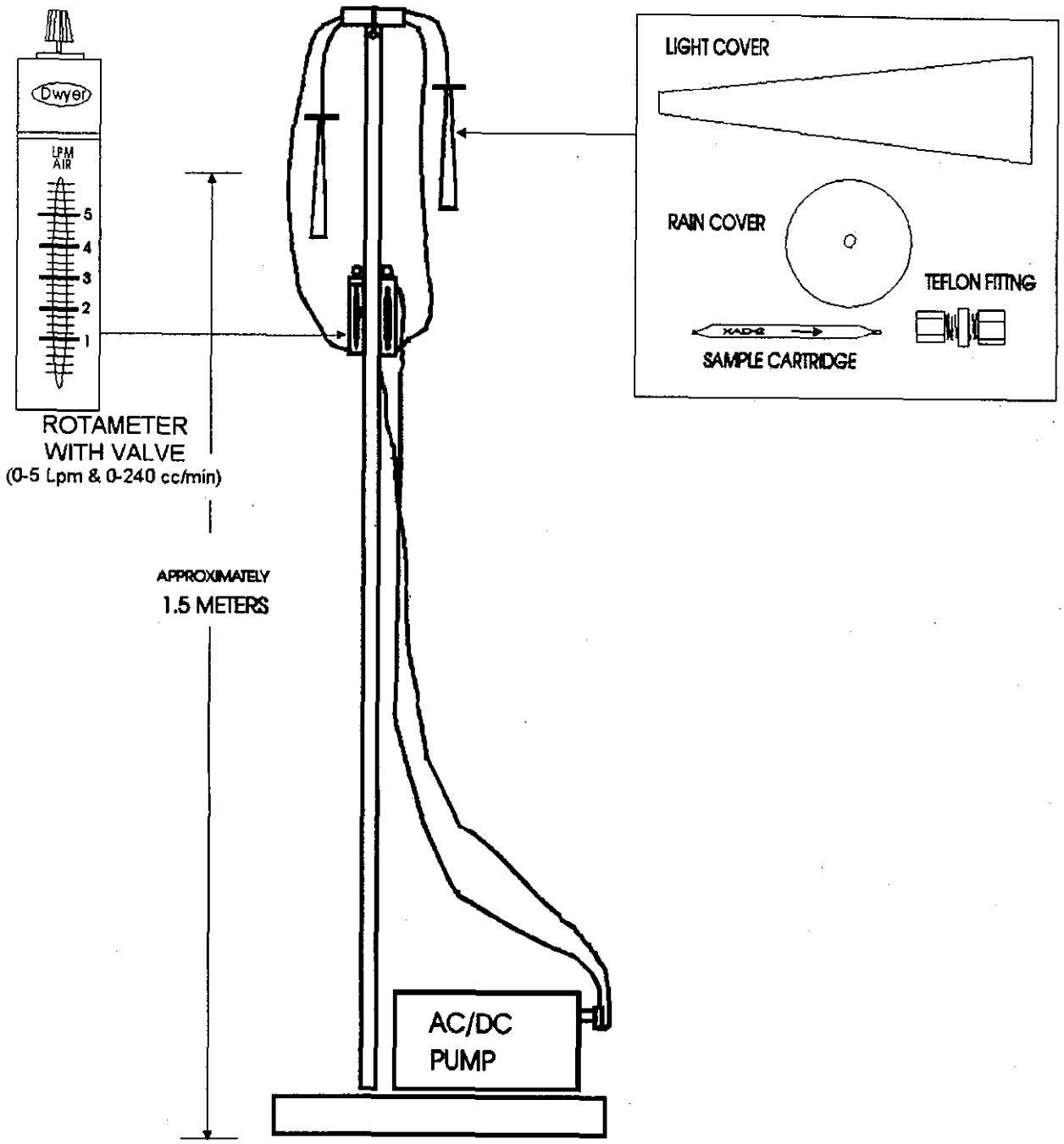


FIGURE 2: SAMPLE TREE WITH TWO ROTAMETERS